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MECHANISM AND CHEMICAL INHIBITION OF THE
HYDRAZINE-NITROGEN TETROXIDE   REACTION

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FOREWORD

ABSTRACT

The mechanism of the hydrazine-nitrogen tetroxide reaction was investigated by examination of the variation in reaction products and equilibrium reaction temperature with increasing reactant concentration when argon-diluted reactant streams were rapidly mixed in a flow reactor. It is concluded that the reaction proceeds through a thermal reaction mechanism rather than a chain-branched explosion mechanism.

An ignition test was devised to determine the effect of candidate reaction inhibitors. No effective inhibitors were found among 27 gaseous and 28 liquid additives tested. Thiophene, toluene, trimethyl borate, ethyl bromide and benzene produced some inhibition, but only at high concentrations. These results support the conclusions that a thermal mechanism is operative.

This technical documentary report has been reviewed and is approved.

WILLIAM C. SAVAGE
Chief, Environmental Branch
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1. INTRODUCTION

As part of a long-range program to elucidate the mechanisms of flame inhibition, research to find effective inhibitors of the hypergolic reaction between hydrazine and nitrogen tetroxide was undertaken. This report describes the results of that investigation. The general approach included:

    1. Literature survey of existing literature on the over-all reaction, and all sub-reactions that might be pertinent in the over-all mechanism.

    2. Definition of the ignition characteristics of the reactant system under inert gas diluent conditions.

    3. Definition of an ignition procedure by which potential inhibitors could be tested for effectiveness in retarding the reaction rate.

    4. Clarification of the preflame reaction mechanism by analytical and spectroscopic techniques.

Since very little was known about the mechanism of the hydrazine-nitrogen tetroxide reaction, a good deal of effort was expended on section 4 above. Although our results have not completely defined the reaction mechanism, we believe a significant advance has been made.

2. SUMMARY

Studies of the hydrazine-nitrogen tetroxide reaction indicate that a thermal reaction mechanism is operative which is initiated and propagated primarily by molecular interaction. No evidence for a chain branching explosion mechanism was found. If this is true, one would not expect small quantities of inhibitor to appreciably decrease the over-all reaction rate. In the chain branched reaction, minute quantities of inhibitor effectively reduce reaction rate through removal of active free radicals from the prereaction zone. In the case of a thermal molecular reaction, only two inhibitor mechanisms exist, both requiring major inhibitor concentrations. The first occurs when the agent competes with one reactant for the other, resulting in a lower net heat release. The second involves

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application of an agent which removes the exothermic heat
of reaction to maintain the equilibrium temperature below
the ignition temperature.

The conclusion, that a thermal reaction mechanism is
operative, is supported by experimental results obtained
in reaction mechanism studies, and investigations of the
effect of candidate inhibitors on the ignition limit of
argon-diluted reactants. In reaction mechanism investi-
gations, the distribution of products and the equilibrated
reaction temperatures resulting from the mixing of argon-
diluted reactants were studied as a function of reactant
concentration. Under dilute conditions, below 2 mole %
of each reactant, a preignition reaction was found to
proceed, yielding as major products ammonium nitrate and
nitrous oxide. At concentrations of 2 mole % and higher
of each reactant, the preignition reaction product analyses
indicated a regular increase in nitrogen and nitric oxide
at the expense of nitrous oxide. At 3 mole % of each
reactant and above, the major gaseous products were nitrogen
and nitric oxide, along with minor quantities of nitrous
oxide and ammonia. At 5 mole % of each reactant spontaneous
ignition occurred, and at 6 mole % the reaction flask was
uniformly enveloped in flame. The experiments were con-
ducted by rapidly mixing the two argon-diluted reactant
streams with a high speed stirrer in an insulated reaction
flask.

The emission spectrum from the nitrogen tetroxide-hydrazine
flame indicated the presence of NH_2, NH and OH radicals
after the flame front. It was not possible to conduct
emission measurements in the preflame region where the
presence of free radicals would imply a chain-branched
reaction mechanism. High speed schlieren movies of the
ignition of a hydrazine droplet in an argon-nitrogen dioxide-
nitrogen tetroxide atmosphere were of qualitative interest,
but offered no quantitative insight into reaction mechanism.

A modified spontaneous ignition technique was employed to
screen 27 gaseous and 28 liquid inhibitor candidates for
the hydrazine-nitrogen tetroxide reaction. Of these,
only five were found to inhibit the hypergolic reaction,
and these to only a small extent. They are thiophene,
toluene, trimethyl borate, ethyl bromide and benzene. No
explanation for their effectiveness can be advanced. The
relative concentration of inhibitor studied was quite
large. It seems reasonable that no inhibitor acting by
removal of a critical intermediate was found for the
hydrazine-nitrogen tetroxide reaction since this type of
inhibition requires a relatively small amount of the active
agent.

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3.   SPONTANEOUS IGNITION CHARACTERISTICS

In preliminary studies, when a high concentration of
nitrogen tetroxide was added to low concentrations of
argon-diluted hydrazine, hypergolic ignition resulted
at room temperature even when only 2 mole % hydrazine
was present. On the other hand, when liquid hydrazine
was admitted to argon-diluted nitrogen tetroxide, there
was found a limiting nitrogen tetroxide concentration
below which spontaneous ignition did not occur at a
given constant temperature. Similar behavior was noted
by the Bureau of Mines (Ref. 1) during spontaneous
ignition measurements on hydrazine-unsym.-dimethyl-
hydrazine (UDMH)-nitrogen tetroxide-air mixtures.

3.1   Inhibitor Screening by Spontaneous Ignition
Limit   It was observed that when a drop of hydrazine,
originally at room temperature, is dropped into an
Erlenmeyer flask filled with an NO_2* (equilibrium-
nitrogen tetroxide-nitrogen dioxide mixture)-argon mixture
at $75^{\circ}C$, spontaneous ignition occurs   when the con-
centration of NO_2* in argon exceeds 11 mole %. If the
mixture contains less than 11 mole % NO_2*, a nonflame
reaction occurs.   These observations agree qualitative-
ly with those of Perlee, Imhof and Zabetakis (Ref. 2)
who found the concentration limit at $75^{\circ}C$ to be 13.2
mole % of NO_2* in air.

A series of experiments were designed by means of which
the effect of selected candidate inhibitors on this
ignition limit could be studied rapidly. It was reasoned
that an effective inhibitor would displace the ignition
limit to higher concentrations of NO_2*.

The apparatus for studying the spontaneous ignition of
a hydrazine drop in an atmosphere containing NO_2* vapor
is presented in Figure 1. Argon, NO_2*, and gaseous
inhibitor are metered through rotameters. The gases
mix and flow into a 250-ml Erlenmeyer flask, thermo-
statted at $75^{\circ}C$ in a water bath. When all air has been
displaced from the flask, gas flow is stopped, and after
30 seconds, during which turbulence in the flask dimin-
ishes, a drop of hydrazine is allowed to fall into the
flask, and results are noted. To enable screening of
vaporized liquids as inhibitors, the apparatus includes
a heated injector. The liquid, fed into the injector
by a variable speed syringe driving motor, is vaporized
in the injector and admitted into the main stream through
a fine slot.

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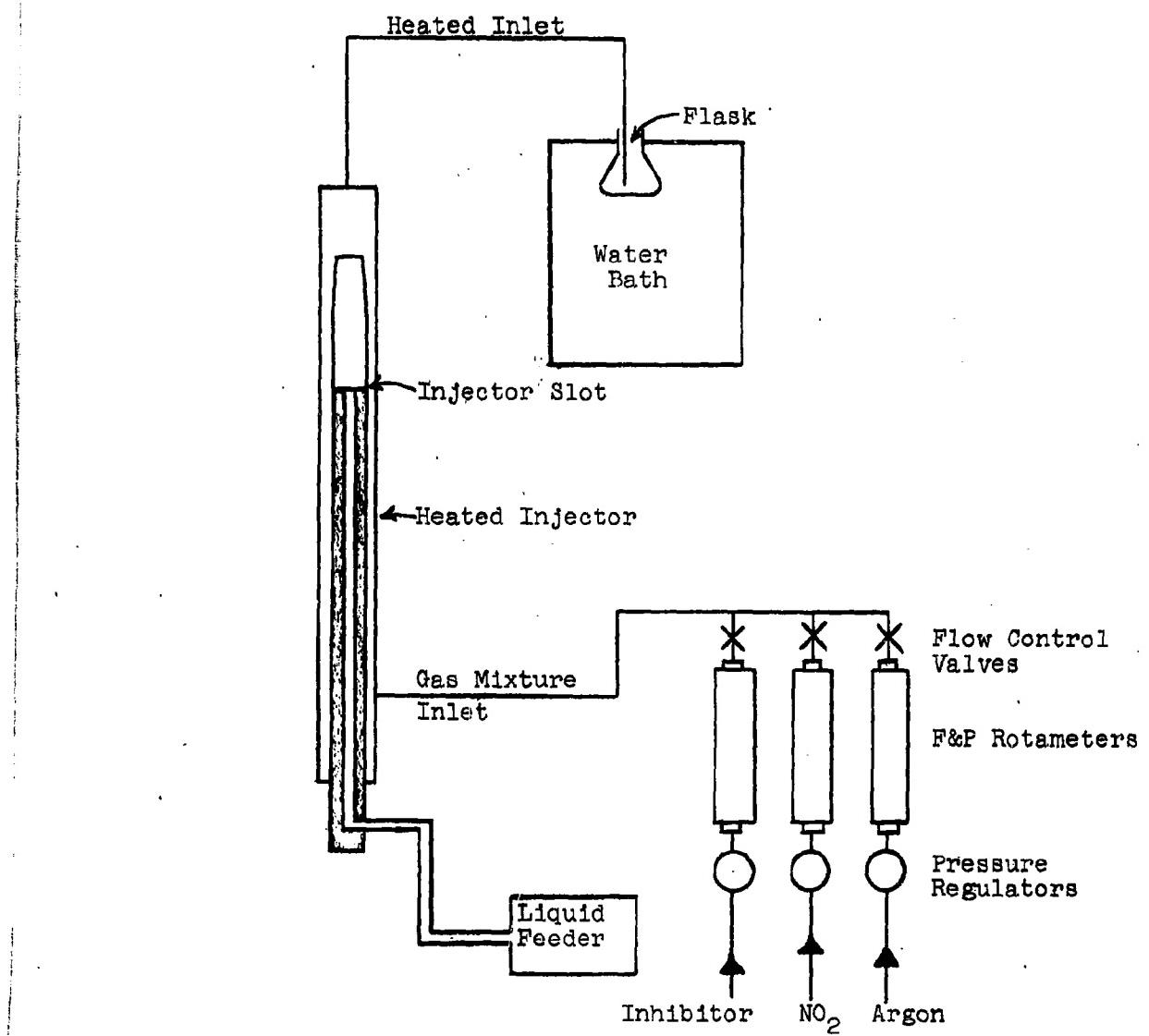
Figure 1. Spontaneous Ignition Apparatus

It was decided that an effective inhibitor might raise the NO_2* concentration ignition limit from 11 mole % to 15 mole %. Therefore, gas mixtures containing 15 mole % of NO_2*, 5% inhibitor and 80% argon were tested. None of the 27 gaseous inhibitors tested prevented ignition under these conditions. Some might have increased the concentration limit slightly above 11% NO_2*, but if so the change was insignificant and no effort was made to check the point. The gaseous inhibitor candidates tested are presented in Table 1.

Table 1. GASES SCREENED AS INHIBITORS OF SPONTANEOUS IGNITION OF HYDRAZINE-NITROGEN TETROXIDE

Methane	1,1-Difluoroethylene
Methyl chloride	n-Butane
Methyl bromide	1,3-Butadiene
Trifluoromethane	Hydrogen bromide
Carbon tetrafluoride	Hydrogen chloride
Bromotrifluoromethane	Hydrogen sulfide
Bromochlorodifluoromethane	Ammonia
Dibromodifluoromethane	Carbon monoxide
Ethyl chloride	Carbon dioxide
Chlorotrifluoromethane	Nitrous oxide
1,1-Difluoroethane	Sulfur dioxide
Dichlorotetrafluoroethane	Sulfur hexafluoride
Ethylene	
Ethylene oxide	
Vinyl chloride	

The liquid inhibitors were tested similarly. The liquids were syringe-driven into the injector, vaporized, and injected into the NO_2*-argon stream through a heated line (to prevent condensation). The mixtures were again 15 mole % NO_2*, 5% additive and 80% argon.

The 28 vaporized liquid candidate inhibitors are presented in Table 2. Of these 8 appeared to be effective.

Table 2. VAPORIZED LIQUIDS SCREENED AS INHIBITORS
OF SPONTANEOUS IGNITION OF HYDRAZINE-
NITROGEN TETROXIDE

Ineffective	Effective
Acetone	Benzene
Acetic acid	Diethyl ether
Acetonitrile	Dimethyl sulfide
Bromobenzene	Ethyl bromide
Bromochloromethane	n-Octane
Carbon disulfide	Thiophene
Carbon tetrachloride	Toluene
Chloral	Trimethyl borate
Chlorobenzene	
Chloroform	
Dibromotetrafluoroethane	
Ethyl iodide	
Iron pentacarbonyl (a)	
Methanol	
Nitromethane	
Phosphorous trichloride	
Silicon tetrachloride	
Tetramethyl lead (a)	
Titanium tetrachloride (a)	
Water	

(a) Plugged inlet tube

Three of the compounds tested (iron pentacarbonyl, tetra-methyl lead, and titanium tetrachloride) reacted with NO_2* to such an extent that they plugged the inlet tube, and could not be properly tested.

To determine their ultimate effectiveness, the inhibitory materials were tested at 5% concentration in mixtures containing greater than 15% NO_2*. The results are listed in Table 3.

Table 3. ULTIMATE EFFECTIVENESS OF INHIBITORS FOR HYDRAZINE-
NO_2* REACTION

Material	Inhibited at, % NO_2* in Mixture	Failed at,
n-Octane [a]	23.8	24.8
Diethyl ether [a]	22.5	23.8
Dimethyl sulfide [a]	22.5	23.8
Thiophene	18.7	19.5
Toluene	18.6	19.6
Trimethyl borate	17.2	18.6
Ethyl bromide	16.4	17.2
Benzene	15.6	17.2

[a] Not actually inhibitors - see text

n-Octane, diethyl ether, and dimethyl sulfide appeared to
react directly with the NO_2*, with considerable heat re-
lease. The hydrazine drop provided enough additional
heat to ignite the NO_2*-inhibitor mixture, after which
no NO_2* remained to burn with hydrazine. With the other
inhibitors, the NO_2* disappeared slowly during the experi-
ment, reacting with hydrazine by the nonflame reaction.
Therefore, these last five materials acted as true inhibi-
tors, though not extremely good ones. The first three
cannot be considered inhibitory.

It can be seen from Table 3 that 5% of inhibitor was
effective in neutralizing no more than 8% of NO_2*. The
inhibiting effects could plausibly result from a prefer-
ential chemical reaction of the inhibitor to remove either
the fuel or the oxidizer, or else by an increase in the
specific heat or heat transfer rate of the gas mixture.
Either of these mechanisms would require a relatively
large amount of added material. It seems reasonable that
no inhibitor acting by removal of a critical intermediate
was found for the hydrazine-NO_2* reaction, since this
type of inhibition requires a relatively small amount of
the active agent.

This reaction is an acid-base reaction, hence proceeds
rapidly to completion. Since the hydrazine-NO_2* reaction
starts spontaneously, its rapid exothermic character
carries the first stage to completion as soon as the
reactants are combined. In view of the high spontaneous
heat release of this reaction and the failure to find any
highly effective inhibitors out of 55 candidates tried,
it seems improbable that any ignition inhibitors exist.

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3.2   The Preignition Reaction   Early in the spontaneous ignition studies it was observed that when the nitrogen tetroxide was sufficiently diluted with inert gas, the hydrazine-nitrogen tetroxide reaction produced ammonium nitrate (solid) and nitrous oxide (gas). The solid product (not previously reported for this reaction) was identified by x-ray diffraction measurements, while gas analysis was obtained by infrared. Because of this reaction premixed flame studies at near-atmospheric pressures could not be carried out.

4.   INVESTIGATION OF THE HYDRAZINE-NITROGEN TETROXIDE FLAME MECHANISM

Since the mechanism of the hydrazine-nitrogen tetroxide combustion process was almost entirely unknown, it was necessary that our research include a study of the un-inhibited reaction. It was hoped that understanding of the mechanism might suggest specific inhibitors not previously tested.

4.1   High Speed Movies of the Ignition of a Drop of Hydrazine   To gain more insight into the ignition process that occurs when a drop of hydrazine falls into NO_2*-argon, high speed movies were taken at about 1500 frames per second. The NO_2*-argon mixture contained 20% NO_2*, and was originally at room temperature, as was the hydrazine. The gas mixture, contained in a 2-inch square glass cell, was viewed through the schlieren system, which made it easier to see flow patterns and density changes. Flow of NO_2*-argon was shut off a few seconds before addition of the hydrazine to avoid gas motion not due to the ignition process.

A sequence of individual frames selected from a 100-ft roll of film (about 4000 frames total) is shown in Figure 2 along with the time in milliseconds after the drop hit the bottom of the glass cell. From these photographs, the ignition process may be divided into seven stages. Stage 1 shows the hydrazine drop entering the glass cell. The tube to the far left is the NO_2*-argon entrance tube and the droplet is about to contact a small glass plate located on the bottom of the cell. Stage 2 illustrates a preignition reaction during which hydrazine vaporizes into the NO_2* atmosphere,

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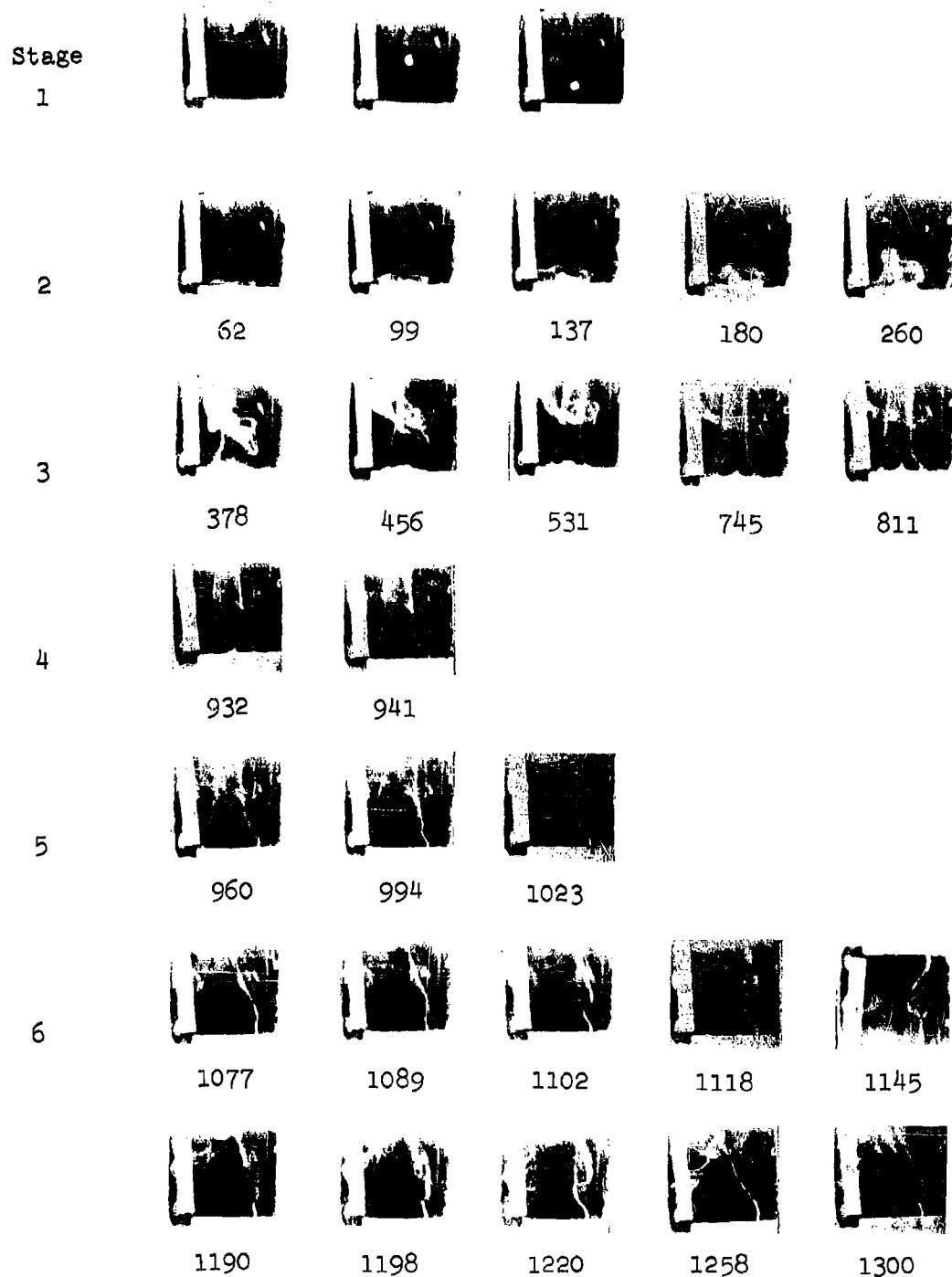
Figure 2. High Speed Photographs of Hydrazine Droplet Ignition
(Numbers refer to time in milliseconds from start of test)

forming a growing particulate cloud of ammonium nitrate. During this time a spherical droplet appears to take form on the glass plate.

From the photographs it is not clear whether ignition occurs at Stage 3 (ca 378 millisec) or at Stage 4 (932 millisec). During Stage 3 what appears to be a flame is formed while the amount of smoke gradually decreases until at 811 millisec only a faint wisp remains. During Stage 3 a conical inner core appears directly on the glass plate surface and becomes sharply defined. This core may represent a surface of reaction or a pool of liquid hydrazine.

An alternate explanation would be that the apparent flame boundaries in Stage 3 represent ammonium nitrate streams which are directed upward due to their low bulk density and under the influence of the exhaust duct located directly above the apparatus. The sudden disappearance of the conical core in Stage 4 would then represent the onset of ignition.

In Stage 5 the reacting surface is established, while Stage 6 follows a representative cycle termed "flicker" of the flame. In this cycle an established surface separates at the base of the flame, gradually lifting off while a new surface is being formed. In Stage 7 the "flicker" of the flame was repeated. The total film time was over 2000 millisec.

So as to clearly define the onset of ignition, the apparatus was modified. A photomultiplier tube was placed perpendicular to the schlieren axis which fed a signal to a trigger circuit. This triggered an intense high voltage spark source in line with the schlieren axis when ignition occurred. The apparatus worked perfectly; however, the mode of ignition appeared nonreproducible, and the experiments were discontinued.

  4.2 Spectroscopic Studies of the Hydrazine-Nitrogen Tetroxide Diffusion Flame The emission spectrum of a hydrazine-nitrogen tetroxide flame produced with the diffusion burner (Figure 3) was studied employing the Jarrell-Ash Model 82000 spectrometer. Argon-diluted streams of nitrogen tetroxide and hydrazine preheated to $85^{\circ}C$ were metered up through the concentric tubes. The spectrum was taken near the top of the yellow rounded inner cone.

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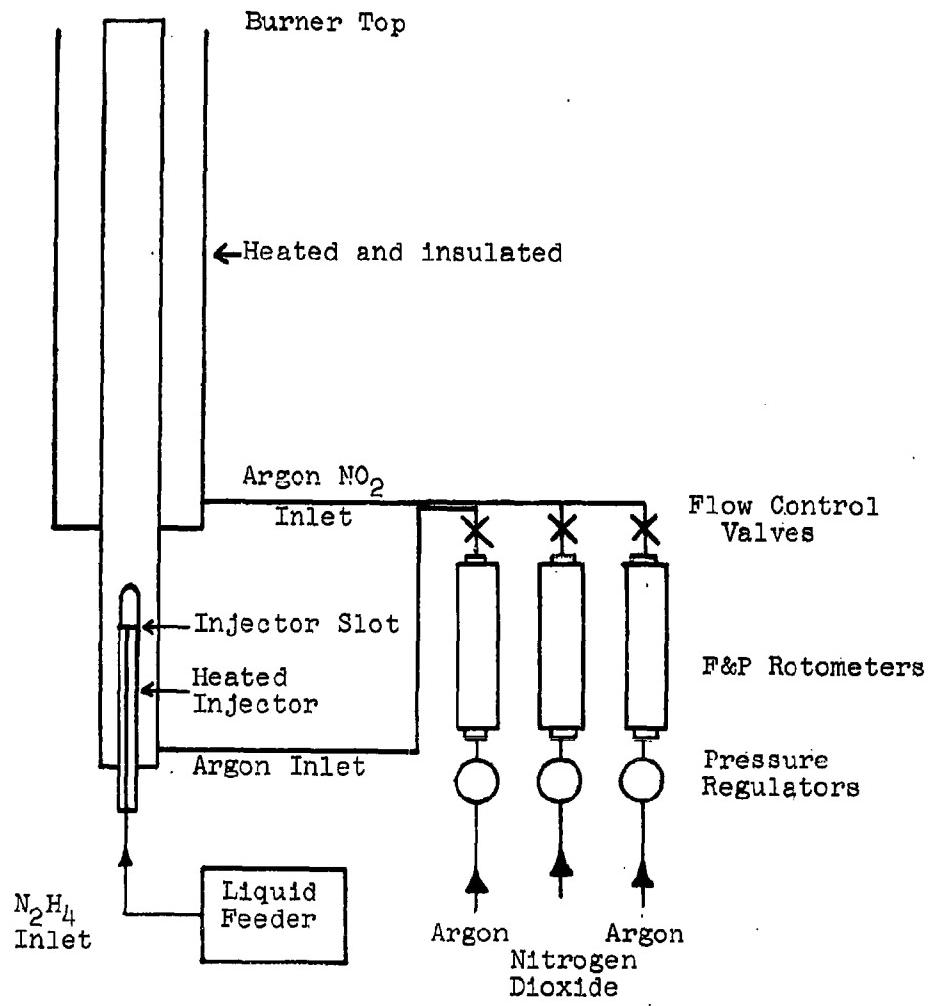
Figure 3. Hydrazine-Nitrogen Tetroxide
Diffusion Flame Burner

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The most important spectral feature was the spread out emission spectrum of NH_2, which extended from about 6000 to 4500 A. In addition, peaks due to NH at 3360A and OH near 3100A were detected. It must be pointed out that the presence of free radicals in the hydrogen-nitrogen tetroxide flame does not constitute proof that the radicals are involved in the ignition process.

4.3   Stirred Reactor Studies - Temperature and Product Analysis   Early work indicated that at low concentrations of nitrogen tetroxide in argon a pre-ignition reaction proceeded when a hydrazine droplet entered the NO_2* atmosphere. At 2.2% NO_2* or below, the reaction was found to proceed in nearly 80% conversion to ammonium nitrate and nitrous oxide according to the reaction

$$N_2H_4 \; + \; N_2O_4 \; \longrightarrow \; NH_4NO_3 \; + \; N_2O$$
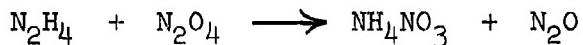
Infrared analysis indicated that nitrous oxide was the only nitrogen oxide formed, and therefore it appeared that some NO_2* was reduced to nitrogen.

While the study of the reaction that occurs when a drop of hydrazine is added to NO_2* vapor offered some insight into the mechanism, this technique has limitations. The roles of diffusion, convection and heat transfer are important but are difficult to evaluate quantitatively. Of the heat generated by the reactions, some is transferred to unreacted gas, some to the container walls, and some to the vaporizing hydrazine, and some, of course, remains in the reaction products, raising their tempera-ture. It was not possible to determine from these experiments just what temperature and what substances were required to bring about the transition from nonflame to flame reaction.

It was desirable to obtain information as to the course of the precombustion reaction up to the point of spontaneous ignition, in the absence of competing physical processes such as vaporization and mixing. A knowledge of the gaseous reaction products and the reaction temperature as a function of initial reactant concentration would lead to a better understanding of the over-all mechanism. Since the argon-diluted reactants could not be premixed without reaction, a method was devised to permit dilute, prevaporized reactant streams to be mixed instantaneously.

A series of experiments was planned which made use of the instrumented diffusion burner previously employed for the spectroscopic study. A stirred reactor was mounted on the exit of the diffusion burner so that concentric streams of hydrazine-argon and NO_2*-argon entered through a hole in the bottom of a 200-cc Pyrex flask, where they were rapidly mixed by a paddle-wheel stirrer. The temperature of the product gases was measured by a chromel-alumel thermocouple. Gas samples at equilibrium were withdrawn through a stainless steel capillary for infrared, mass spectrometric and gas chromatographic analysis. The flask was well insulated with asbestos. At higher reactant concentrations it was necessary to substitute a quartz flask since the equilibrated temperature surpassed the temperature capability of Pyrex. The stirred reactor is sketched in Figure 4.

In this reactor, streams of nitrogen dioxide and hydrazine in argon, preheated to 85°C, were rapidly mixed as they entered the flask. After a short period during which the flask and stirrer warmed up, the reactor came to a steady state, with a constant product gas temperature and composition. Employing this method, experiments were conducted in which the nitrogen dioxide and hydrazine streams were at the same concentration in mole per cent, but this concentration was successively increased from 2% nitrogen dioxide - 2% hydrazine - 96% argon to 6% of each reactant and 88% argon.

The gas products were analyzed by one or more of the three analytical techniques used: infrared, mass, or VPC; thus, nitric oxide was analyzed by all three methods, while hydrogen was analyzed only by gas chromatography.

Results by different methods, when used, agreed within the expected accuracy ranges, and average values are therefore reported.

The gaseous product analysis in mole per cent and the temperature rise in °C for each experiment are presented in Table 4. In the experiments at 4.5, 5.0, and 6.0% reactants, it was first observed that rate of stirring affected the extent of reaction and the final equilibrated temperature. A setting on the variable speed motor was found at which the highest temperature was observed; any change in the stirring speed would lower the equilibrated temperature. For these experiments the analysis and temperature reported correspond to that stirring speed at which the temperature was maximum. The analyses completely neglect the quantities of any condensed phase products such as water and ammonium nitrate. No attempt was made to determine these species.

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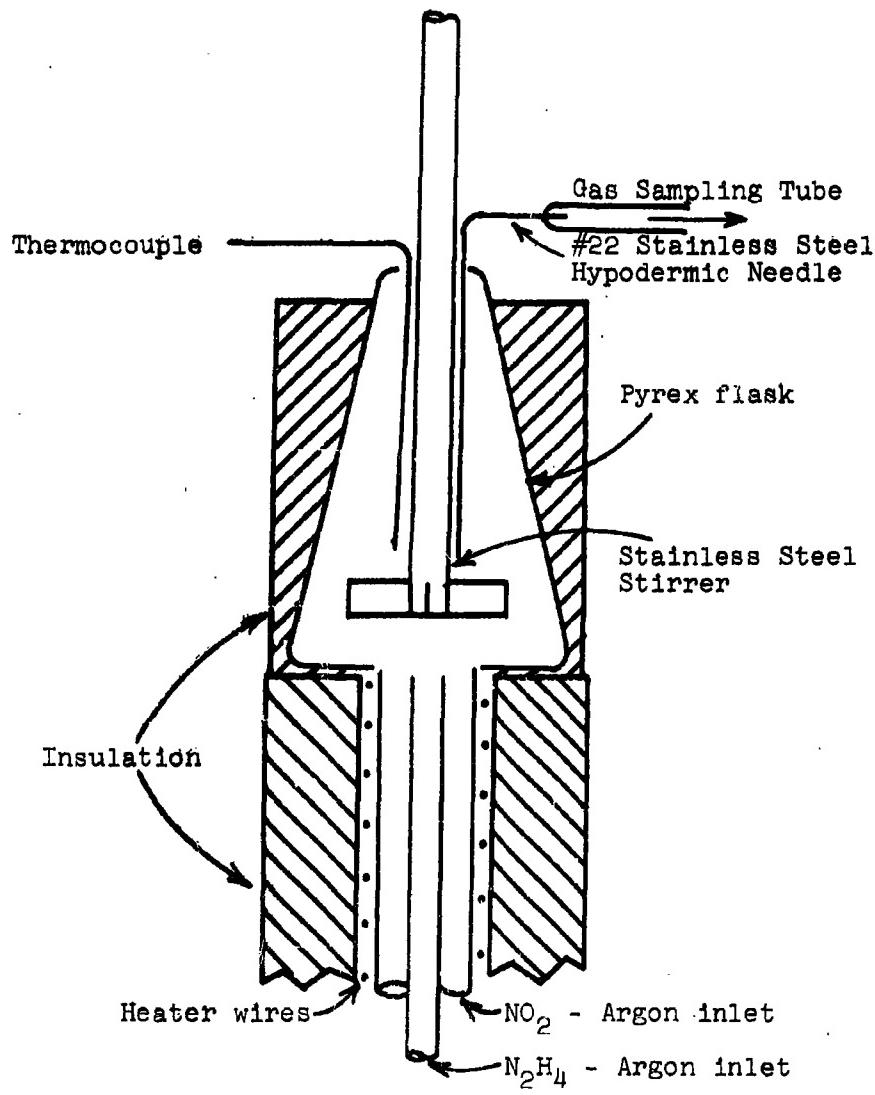
Figure 4: Stirred Reactor for Hydrazine-Nitrogen
Tetroxide Ignition Studies

Table 4. GAS PRODUCT ANALYSIS AND EQUILIBRIUM TEMPERATURE RISES FOR ARGON-DILUTED HYDRAZINE-NITROGEN DIOXIDE STIRRED REACTIONS

Mole % of Each Reactant	2.0	3.0	3.0	3.5	4.0	4.0	4.5	5.0	6.0
Temperature Rise, °C	109	238	237	315	468	542	606	737	843
Mole % Products									
N_2O	0.70	0.24	0.22	0.16	0.29	0.16	0.10	0.23	0.24
N_2	1.68	3.79	4.13	5.15	6.06	6.92	(a)	7.98	8.75
NH_3	- (b)	0.25	- (b)	0.68	0.23	0.72	- (a)	- (b)	- (b)
NO	1.66	3.93	3.78	3.79	4.39	2.80	- (a)	3.16	4.73
H_2	0.022	0.11	0.10	0.21	0.44	0.91	- (a)	0.95	0.61

(a) Product analysis prevented by air leak into samples.

(b) No NH_3 present.

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The nonflame reaction continued at reactant concentrations below 5 mole %. At 5 mole % a very dim flame was observed, and at 6% reactants the flame appeared to fill the entire reactor. Product analysis indicates that at 6% reactants the reaction is not yet complete according to the reaction

$$NO_2 \; + \; N_2H_4 \longrightarrow 2H_2O \; + \; 3/2 \; N_2$$

This is supported by the measured temperature rise of $737^{\circ}C$ for the 5% reactant experiment, compared to the calculated temperature rise of $1244^{\circ}C$ for complete reaction. Thus the actual value represents an efficiency of only 60%. The maximum change of temperature with reactant concentration was found to occur between 3.5 and 4.0% of reactants. At about 3.8% reactants the indicated temperature from the thermocouple constantly fluctuated between two extremes. In one case the fluctuation was rapid between $438^{\circ}C$ and $597^{\circ}C$ (these temperatures include a preheat of $85^{\circ}C$). This behavior indicates a change in reaction mechanism. That is, at 3.8% reactants, or at about $440^{\circ}C$, a new reaction is just at the threshold of asserting itself in the overall reaction mechanism.

The data of Table 4 can be more realistically presented by calculating the per cent of total gas phase nitrogen appearing in each of the gaseous products. Data so calculated more clearly represent the approach to the complete reaction. Consider, for example, a product mixture which contains equal quantities of nitrogen and nitrous oxide. As far as the complete reaction is concerned, where all nitrogen atoms appear as nitrogen gas, the reaction is 67% complete. The results of these calculations are illustrated in Figure 5 where the mole per cent of product gases based on their nitrogen atom content is plotted against the per cent of each reactant in the argon-diluted streams. In addition the equilibrium temperature rise is illustrated for each experiment.

The data are not completely consistent, but the trend with increasing reactant concentration is readily apparent:

1. The proportion of nitrogen and hydrogen gas to the remaining gaseous products increases with temperature or concentration.

2. The proportion of nitrous oxide decreases with temperature to a low constant value.
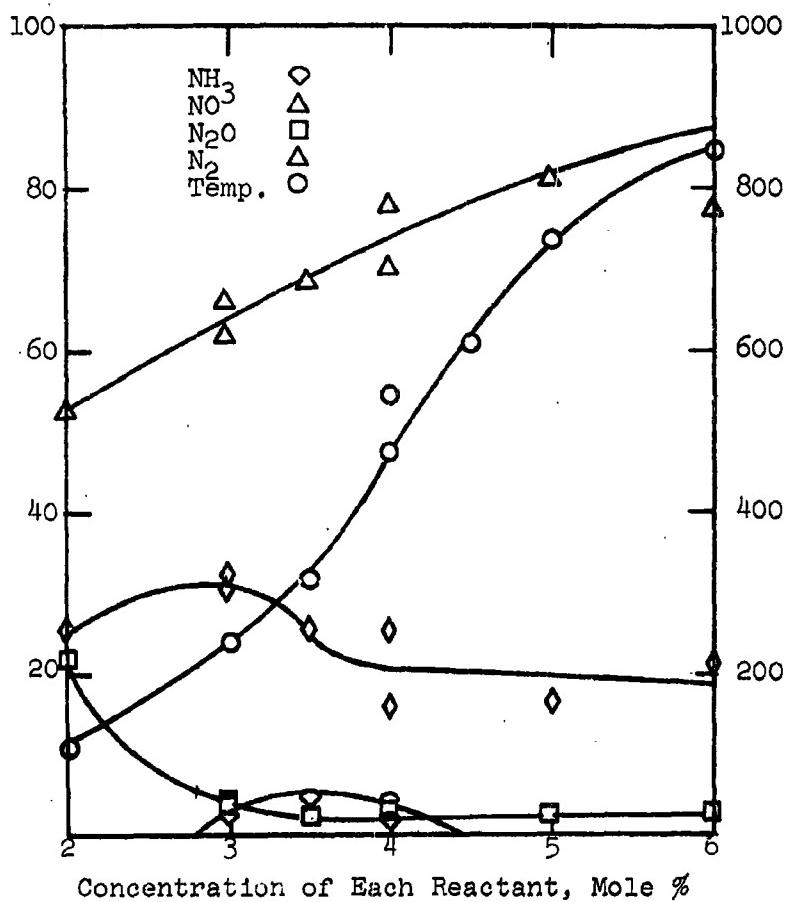
Figure 5. Equilibrium Temperature Rise and Product
Distribution as a Function of Reactant
Concentration in the Stirred Reactor

3. The proportion of nitric oxide first increases and then decreases with temperature.

4. The quantity of ammonia increases to a maximum and then decreases.

5. The major gaseous products above 3% reactants are nitrogen and nitric oxide.

5. CONCLUSIONS AND RECOMMENDATIONS

The pattern of combustion product distribution and reactant temperatures furnished by the stirred reactor investigations suggests that the over-all reaction mechanism is complex. To appreciate this fully, potential competing reactions are listed in Table 5, along with their heats of reaction at 25°C.

In the following paragraphs the information available on the individual reactions is discussed, with the objective of explaining which would be important in the over-all reaction. The temperature at which the reaction rate becomes sufficiently rapid that an appreciable fraction of the reactants would be used up in one second was considered the critical property. These temperatures, listed in Table 5, are those above which the reactions are rapid enough to play a part in the ignition process.

Reaction N-1   Initially the only oxidizers present are nitrogen dioxide and nitrogen tetroxide. They are in dynamic equilibrium, with about 50% of the latter dissociated at room temperature and pressure (Ref. 3). At 75°C the dissociation of nitrogen tetroxide is 95%, and this percentage increases steeply with temperature. Therefore, as the reactions occur and heat the gas as high as 140°C (Ref. 4), nitrogen tetroxide converts almost quantitatively to nitrogen dioxide. Since ignition occurs only at much higher temperatures, one can rule out nitrogen tetroxide reactions as its cause.

Reaction N-2   The initial reaction between nitrogen dioxide and hydrazine to yield nitrous oxide, ammonium nitrate, and a considerable amount of heat is definitely known to occur at room temperature even when the partial pressure of the reactants is less than 0.01 atmosphere.

Table 5. KNOWN AND POSSIBLE SUB-REACTIONS IN THE
HYDRAZINE-NITROGEN TETROXIDE REACTION

No.	Reaction (All substances are taken as gases unless otherwise noted)*	Heat of Reaction at 25°C, Kcal per g mol of First Reactant in Equation
N-1	$N_2O_4 \underset{\longleftarrow}{\overset{140°}{\longrightarrow}} 2\ NO_2$	+ 13.9
N-2	$N_2H_4\ (liq.) + 2NO_2 \xrightarrow{\leq 25°} N_2O + NH_4NO_3(sol.)$	- 95.8
N-3	$NH_4NO_3\ (solid) \xrightarrow{400°} N_2O + 2H_2O$	- 8.6
N-4	$N_2H_4\ (liquid) \xrightarrow{600°} NH_3 + 1/2\ N_2 + 1/2H_2$	- 23.0
N-5	$NO_2 \xrightarrow{920°} NO + 1/2\ O_2$	+ 13.5
N-6	$NO \xrightarrow{>1350°} 1/2\ N_2 + 1/2\ O_2$	- 21.5
N-7	$N_2O \xrightarrow{1100°} N_2 + 1/2\ O_2$	- 19.6
N-8	$N_2H_4\ (liq.) + 2N_2O \xrightarrow{760°} 3N_2 + 2H_2O$	-166.8
N-9	$NH_3 + 3/2\ N_2O \xrightarrow{950°} 2N_2 + 3/2\ H_2O$	-105.1
N-10	$H_2 + N_2O \xrightarrow{750°} N_2 + H_2O$	- 77.4
N-11	$NH_3 + 5/2\ NO_2 \longrightarrow 7/2\ NO + 3/2\ H_2O$	- 15.4
N-12	$H_2 + NO_2 \xrightarrow{\sim 500°} NO + H_2O$	- 44.3
N-13	$N_2H_4\ (liq.) + 2NO \longrightarrow 2\ N_2 + 2H_2O$	-170.6
N-14	$NH_3 + 3/2\ NO \longrightarrow 5/4\ N_2 + 3/2\ H_2O$	-108.0
N-15	$H_2 + NO \xrightarrow{>1500°} 1/2\ N_2 + H_2O$	- 79.3
N-16	$N_2H_4\ (liquid) + O_2 \longrightarrow N_2 + 2H_2O$	-127.7
N-17	$NH_3 + 3/4\ O_2 \xrightarrow{650°} 1/2\ N_2 + 3/2\ H_2O$	- 75.8
N-18	$H_2 + 1/2\ O_2 \xrightarrow{575°} H_2O$	- 57.8

* All temperatures in degrees centigrade.

Reactions N-3 and N-4   Reaction N-3, the thermal decomposition of ammonium nitrate, and reaction N-4, the thermal decomposition of hydrazine, are known to occur below the over-all ignition temperature and are almost certainly involved in the ignition process. Extrapolation of published data (Ref. 5) shows that Reaction N-3 will go to 99% completion in one second at 410°C. Data on Reaction N-4 (Ref. 6) indicate that this reaction should go to 99% completion in one second at 598°C. Since Reactions N-2, -3, and -4 are all exothermic, they raise the temperature considerably.

Reactions N-5, N-6 and N-7   As the temperature rises, other thermal decomposition reactions of the oxidizers become possible, as indicated by sub-reactions N-5, -6 and -7 in Table 5. One must also consider the possibility of the disappearance of each of the nitrogen oxides by thermal decomposition.

Reaction N-5   From a consideration of thermodynamics the thermal decomposition of nitrogen dioxide to nitric oxide and oxygen (Reaction N-5) is nearly quantitative at 600°C (Ref. 7). Kinetically this second order reaction only goes to 64% completion in one second at this temperature with a partial pressure of nitrogen dioxide of 0.10 atmosphere; at 920°C, Reaction N-5 is 99% complete in one second (Ref. 8).

Reaction N-6   Nitric oxide, formed by the decomposition of nitrogen dioxide, is thermally very stable. The thermal decomposition of nitric oxide (Reaction N-6) goes only to 13% completion in one second for a gas sample at 1347°C, containing 0.10 atmosphere partial pressure nitric oxide (Ref. 9). This reaction is zero-order at temperatures below 1100°C, second order in the 1400-1800°C range, and both mechanisms are involved in the 1100-1400°C range (Ref. 10). Potter and Wayman (Ref. 11) state that even at 2400°K thermal decomposition of nitric oxide is so slow that the reaction is unlikely to contribute to a flame front.

Reaction N-7   Nitrous oxide is also very stable thermally; at temperature of 971°C, 99% of the nitrous oxide initially present at 0.10 atmosphere partial pressure would decompose in ten seconds and at 1104°C, 99% conversion would be obtained in one second (Ref. 12).

Reactions N-8 and N-18   The sub-reactions sus-
pected to occur in the preignition period could produce
several fuels and oxidizers not initially present, the
fuels being ammonia and hydrogen, and the oxidizers
being nitric oxide, nitrous oxide and oxygen. These
possibilities are expressed in sub-reactions N-8 through
N-18 in Table 5.

Reaction N-8   No data for reaction of nitrous
oxide with hydrazine were found, so attempts were made
to measure the autoignition temperature of this reaction
with the standard ASTM apparatus. The procedure of
dropping hydrazine into nitrous oxide-argon atmospheres
was tried but was not successful. At elevated tempera-
tures, sudden vaporization of hydrazine created a local
high concentration which burned, but whether ignition
began in the flask or in the air was not apparent. A
droplet of hydrazine in air will spontaneously ignite
at temperatures as low as $270^{\circ}C$ (Ref. 2). Therefore
experiments were carried out in which a continuous gas
stream containing argon, nitrous oxide, and vaporized
hydrazine was passed into the spontaneous ignition
apparatus. The mixtures tried contained 0.5, 1.0, and
2.0 times the stoichiometric amounts of hydrazine with
4 and 8% nitrous oxide. Also an undiluted mixture, 23%
hydrazine, 77% nitrous oxide, was tried. None of these
mixtures ignited even at temperatures as high as $760^{\circ}C$
(the upper temperature limit of the apparatus). At this
high temperature, hydrazine thermally decomposes rather
rapidly to ammonia, nitrogen and hydrogen. This strongly
suggests that at these concentrations neither ammonia nor
hydrogen are reactive toward nitrous oxide below $760^{\circ}C$.
At other concentrations, as indicated below, nitrous
oxide and hydrogen will react at this temperature.

Reactions N-9 and N-10   Concerning the reaction
of ammonia and nitrous oxide, Destriau and Laffitte re-
ported that one part ammonia mixed with six parts of
nitrous oxide at a combined partial pressure of 100 mm
ignited at a temperature of $950^{\circ}C$ (Ref. 13). A mixture
of 30 mm of nitrous oxide plus 10 mm of hydrogen ignited
when heated to $750^{\circ}C$ (Ref. 14).

Reactions N-11 and N-12   Two additional possible
sub-reactions of nitrogen dioxide should be considered,
one with ammonia and the other with hydrogen. No pub-
lished data was found for the former system. For the

system nitrogen dioxide-hydrogen, Ashmore and Levitt
(Ref. 15) reported that these gases ignite above $500^{\circ}C$,
and that this reaction is inhibited by the presence of
nitric oxide, oxygen and nitrogen and inert gases, but
is slightly accelerated by the presence of water vapor.
Oxygen, the most effective inhibitor, reduces the initial
rate of reaction about 50% when present at 0.5 atmospheres
partial pressure.

Reactions N-13, N-14 and N-15   Though nitric
oxide may potentially react with hydrazine, ammonia and
hydrogen, data on the first reaction are not yet avail-
able. The reaction of hydrogen with nitric oxide
(Reaction N-15) is very hard to initiate as evidenced
by the fact that nitric oxide is stable in nitrogen
dioxide-hydrogen flames at temperatures as high as
$1500^{\circ}C$ (Ref. 16, 17). Reaction N-14 between ammonia and
nitric oxide, is only somewhat less difficult to initiate
(Ref. 18). Heating ammonia to about $2000^{\circ}C$ causes de-
composition, forming NH and NH_2 radicals. These radicals
then react with nitric oxide, but the nitric oxide is not
completely consumed unless ammonia, and thus NH and NH_2,
is present in excess. These last two sub-reactions can
almost certainly be ruled out as contributing to ignition
of hydrazine-nitrogen dioxide.

Reactions N-16, N-17 and N-18   Oxygen, a good
oxidizer, reacts with hydrazine, ammonia and hydrogen
at relatively low temperatures. The ignition tempera-
ture of hydrazine in air has already been stated to be
only $270^{\circ}C$ (see Reaction 8), which is $300^{\circ}C$ below its
decomposition temperature. The minimum ignition tempera-
tures of hydrogen and ammonia in air are $575^{\circ}C$ and $650^{\circ}C$
respectively (Ref. 19). Thus, although these reactions
were considered, they probably do not play a role in
hydrazine ignition in NO_2*, because there is no oxygen
present.

Figure 6 diagrams the possible reaction sequences dis-
cussed above. The results of the stirred reactor studies
can now be interpreted in light of Table 5 and Figure 6.
Ignition occurred at a temperature greater than $690^{\circ}C$
and less than $817^{\circ}C$. These temperatures correspond to
the sums of the temperature rise and preheat temperatures
for experiments at 4.5% and 5.0% of both reactants, or
the concentrations just before and after spontaneous
ignition occurred.
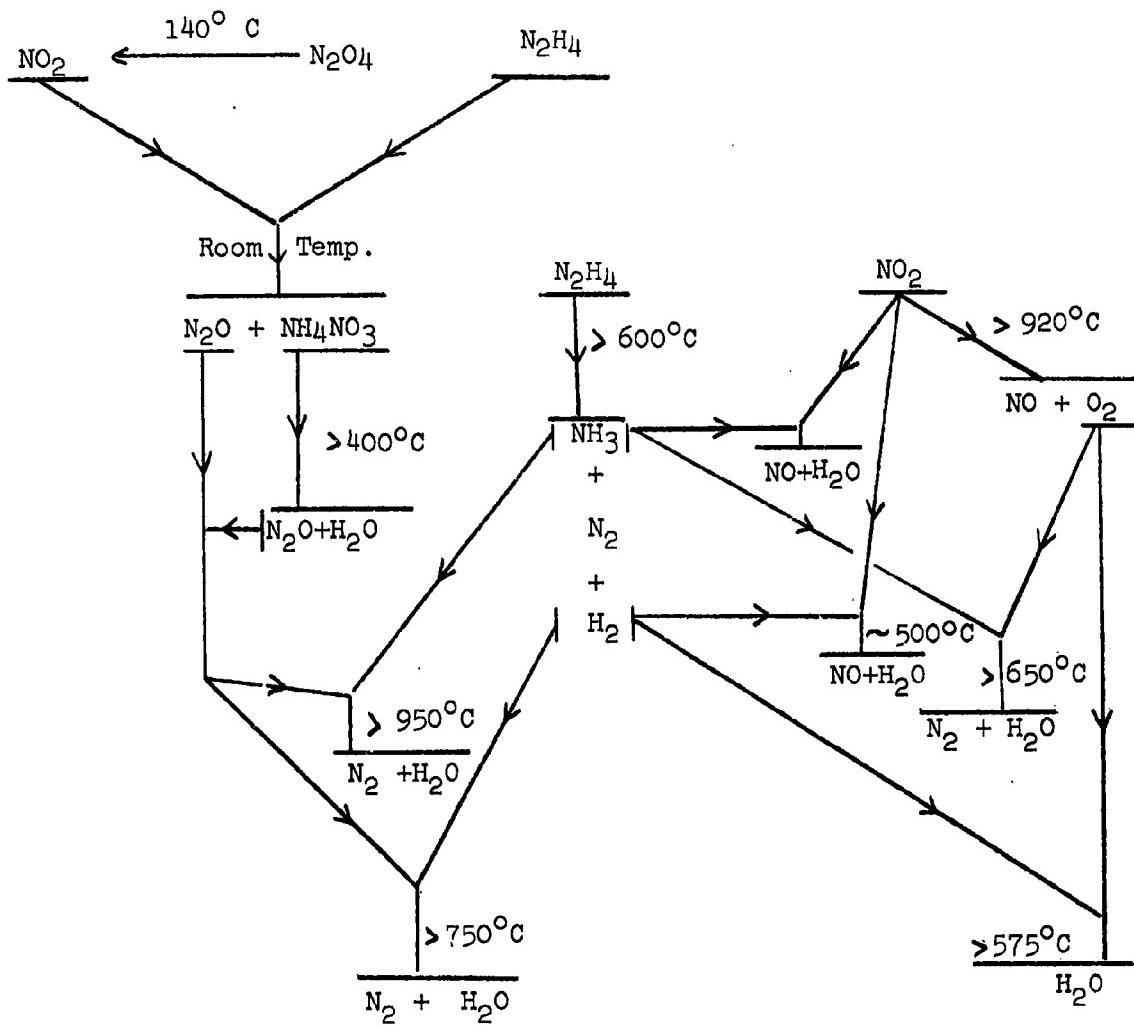
Figure 6. Possible Reaction Sequences in Hydrazine-Nitrogen
Tetroxide Flame Reaction

The species present just before the ignition temperature
is reached are nitrous oxide, nitrogen, nitric oxide,
hydrogen and water, since at $400^{\circ}C$ all the ammonium
nitrate would have decomposed. These products are all
stable toward decomposition up to at least $1100^{\circ}C$ where
nitrous oxide decomposition to $N_2 + 1/2\ O_2$ is 99% complete
in one second. From the analysis of the products at 2%
reactants, and from earlier investigations of preignition
reaction at lower concentrations it seems likely that the
initiating reaction is Reaction N-2

$$2NO_2 + N_2H_4 \longrightarrow N_2O + NH_4NO_3$$
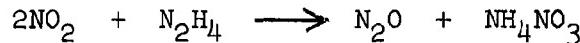
That this equation does not completely account for the
reaction at low reactant concentrations is evident due
to the presence of large quantities of nitric oxide and
nitrogen in the 2% investigation, and the sudden decrease
in nitrous oxide concentration at 3 mole per cent reactants.
In this concentration region both nitric oxide and nitrogen
have increased at the expense of nitrous oxide, while
copious quantities of ammonium nitrate are still observed
as white particulate smoke issuing from the reactor. In
this region, therefore, the initial reaction between
nitrogen dioxide and hydrazine must be producing nitric
oxide and nitrogen as well as nitrous oxide and ammonium
nitrate. This is presented as a mechanism for nitric
oxide and nitrogen formation since none of the sub-
reactions presented in Table 5 will account for nitrogen
and nitric oxide at temperatures in the order of 200 to
$300^{\circ}C$. The initiating reaction above 2% reactants is
therefore considered to result from molecular interaction
of nitrogen dioxide and hydrazine as a type of Lewis
acid-base reaction with the formation of ammonium nitrate,
nitrogen, nitric oxide and nitrous oxide. The relative
concentration of nitrous oxide from the initial reaction
then drops off at the higher temperatures encountered at
3 mole % reactants. Consideration of the temperatures
required for depletion of nitrous oxide by Reactions N-7,
N-8, N-9, and N-10 emphasizes the fact that as the
reaction temperature is increased the initiating reaction
yields a product distribution with very little nitrous
oxide, since this oxide cannot react by any sub-reaction
considered.

When one calculates the heat given off by Reaction N-2,
a temperature rise of approximately $100^{\circ}C$ per 1% increase
in reactant concentration is predicted. The experimental
values at 2% and 3% fall far short of this since one would
expect temperature rises of 200 and $300^{\circ}C$ rather than 109

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and 236°C. Any change in the product distribution where the concentration of nitric oxide and nitrogen is increased at the expense of nitrous oxide or ammonium nitrate would tend to decrease the expected temperature since the heats of reaction would be lower. The experimental temperatures and the gas compositions therefore are in rough agreement.

As mentioned earlier, an apparent change in reaction mechanism occurs at 3.8 mole % reactants where the largest rate of temperature rise with increased composition occurs. This was observed experimentally as a temperature fluctuation between about 440°C and 600°C as the reactor was warming up. This fluctuation is equivalent to temperature rises between 355°C and 520°C. Unfortunately no traumatic change in the over-all gas composition is apparent at this point. This temperature region is where the exothermic decomposition of ammonium nitrate would occur. Since, at this temperature, nitrous oxide cannot be removed by Reactions N-7, N-8, N-9 or N-10, and no increase in nitrous oxide concentration is observed, it is concluded that ammonium nitrate must decompose to a mixture of water, nitrogen and nitric oxide, or even water, nitrogen and oxygen. This decomposition path is more exothermic than that of Reaction N-3 and might furnish the thermal energy necessary for initiation of reactions such as N-4, N-11 and N-12, the exothermic decomposition of hydrazine and reaction of nitrogen dioxide with the resultant hydrogen and ammonia to form water, nitric oxide and nitrogen. If ammonium nitrate is present as a vapor, the exothermic nature of N-3 would be further enhanced.

The nonflame reaction is therefore pictured to be a thermal reaction mechanism, originally initiated by the molecular collision of nitrogen dioxide and hydrazine molecules. As the concentrations of reactants are increased, the mechanism of reaction changes since more exothermic heat is available for initiation of further sub-reactions. This trend increases until at 5 mole % reactants the mixture becomes hypergolic.

The inhibition of a thermal reaction mechanism of this type is virtually impossible since there exists no pre-reaction zone during which critical concentrations of free radicals must build up in order to establish a self-supporting free radical chain mechanism as is the case for hydrogen-oxygen reactions. In this case small quantities of inhibitors,which remove the free radicals from the reactant stream before the flame front,are extremely effective in moderating the reaction. In the

case of nitrogen dioxide-hydrazine, the formation of
nitrous oxide and ammonium nitrate as the initiating
reaction predominant at high dilutions results in a
heat of reaction which is about 2/3 of the heat of re-
action based on one mole of hydrazine for the over-all
desired result:

$$N_2H_4 \;+\; NO_2 \;\longrightarrow\; 3/2 \; N_2 \;+\; 2H_2O \qquad (N-19)$$
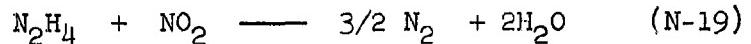
In view of this, and the failure to find any highly
successful inhibitors out of 55 candidates tested, it
seems improbable that effective inhibitors exist for the
nitrogen tetroxide-hydrazine reaction.

Preliminary plans have been completed for construction of
a low pressure burner similar to that designed by Wolfhard
and coworkers (Ref. 20). This burner (Figure 7) will
permit flame studies of premixed gas systems which cannot
be investigated at atmospheric pressure due to hypergolic
tendencies, preignition solid adduct formation, or burner
clogging by solid reaction products. Although the burner
is primarily intended for other reacting systems, it
should be ideal for the study of nitrogen tetroxide-
hydrazine flames. Spectroscopic studies of the flame in
the region before the flame front should afford valuable
information concerning the existence of free radicals in
the preflame region. In addition, the five vaporized
additives which appeared to have some influence on the
composition ignition limit of NO_2*-hydrazine mixtures can
be tested as to their ability to inhibit the premixed
flame velocity of the system.

It is recommended that the research outlined above be
conducted in hope that the reaction mechanism and the
possibility of inhibition be further defined.
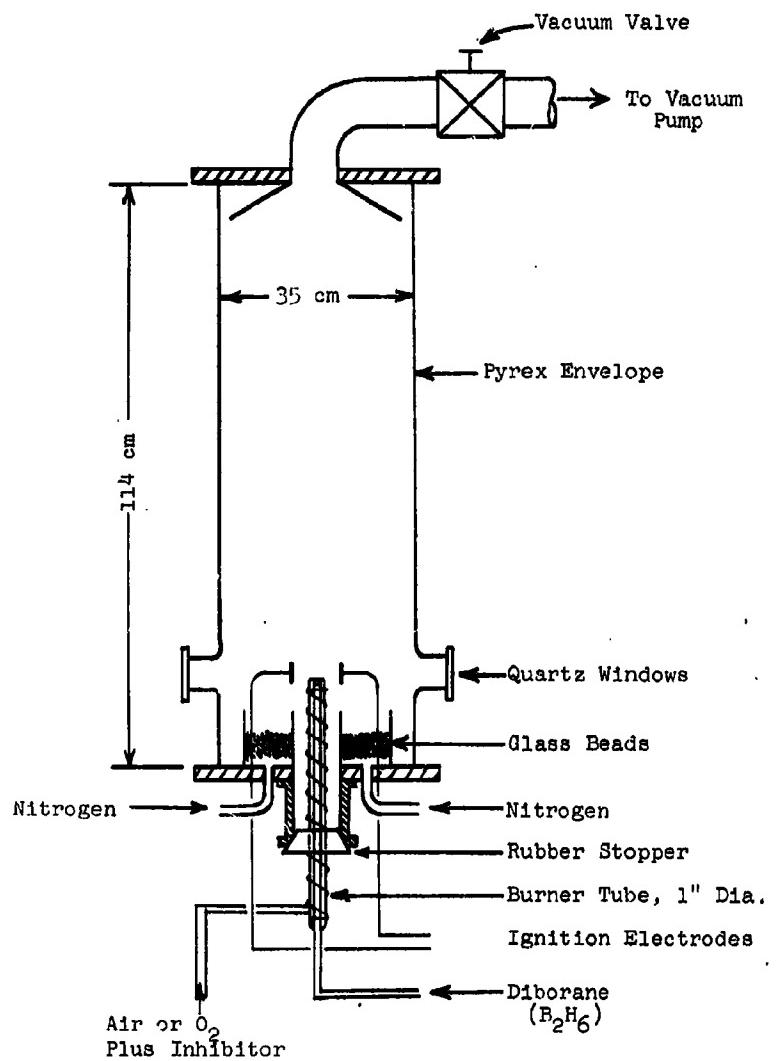
Figure 7. Low Pressure Burner, after Wolfhard (Ref.20)

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Aeronautical Systems Division, Dir/Aeromechanics,
Flight Accessories Lab, Wright-Patterson AFB, Ohio.
Rpt. No. ASD-TDR-62-1041. MECHANISM AND CHEMICAL
INHIBITION OF THE HYDRAZINE-NITROGEN TETROXIDE
REACTION. Final report, Dec 62, 29p. incl illus.,
tables, 20 refs.
                    Unclassified Report

The mechanism of the hydrazine-nitrogen tetroxide
reaction was investigated by examination of the
variation in reaction products and equilibrium
reaction temperature with increasing reactant con-
centration when argon-diluted reactant streams
were rapidly mixed in a flow reactor. It is con-
cluded that the reaction proceeds through a thermal
reaction mechanism rather than a chain-branched
explosion mechanism.

An ignition test was devised to determine the
effect of candidate reaction inhibitors. No
effective inhibitors were found among 27 gaseous
and 28 liquid additives tested. Thiophene, toluene,
trimethyl borate, ethyl bromide and benzene pro-
duced some inhibition, but only at high concentra-
tions. These results support the conclusions that
a thermal mechanism is operative.